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(54) A process for the manufacture of fibre reinforced shaped articles.

(57) In a process for the manufacture of fibre reinforced shaped articles with a matrix of cured inorganic binder (e.g. portland cement), by preparing an aqueous pulp of reinforcing and retentive fibres, subsequently preparing an aqueous slurry of hydraulic inorganic binder particles, reinforcing and retention fibres by suspending hydraulic inorganic binder particles in the pulp, dewatering the aqueous slurry and finally curing the dewatered product, colloidal hydrophilic inorganic particles (e.g. colloidal silica and clay particles) are dispersed in the pulp in order to provide improved dispersion of the fibres in the slurry, improved dewatering properties of the slurry and improved strength of the cured product.

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EP 0 047

A PROCESS FOR THE MANUFACTURE OF FIBRE  
REINFORCED SHAPED ARTICLES

The present invention relates to a process for the manufacture of fibre reinforced shaped articles with a matrix of cured inorganic binder comprising the steps of

5. preparing an aqueous slurry of reinforcing fibres, retention fibres, hydraulic inorganic binder particles and possibly other additives containing an excess of water in relation to the amount necessary to secure hydration of the inorganic binder,
10. forming green shaped articles by dewatering the slurry, and curing the green shaped articles.

It is known to use a number of different types of fibres in the manufacture of fibre reinforced shaped articles, such as sheets and boards used in the building material sector. One of the most important examples of products of this type is asbestos cement products.

15. 20. The most common technologies used by the manufacture of such products are known as the Hatschek method and the Magnani method.

25. It is a common feature of these methods and other less frequently used methods, like the Head Box method and the Fourdrinier method, that they comprise the three above steps: initially preparing an aqueous slurry of cement particles and asbestos fibres, subsequently forming green shaped articles by dewatering, excess water being sucked away, and finally curing the green shaped articles to the final products, e.g. by heat curing, autoclaving or at room temperature.
30. According to the Magnani-method a slurry is used

having a relatively low W/S ratio, i.e. weight ratio water to solid material, usually in the range 1-2. This rather thick slurry is applied directly on an endless permeable belt providing the form desired for the sheet, dewatering being performed by combined suction and compression.

According to the Hatschek method a primary aqueous slurry having a W/S ratio equal to about 2 is formed, this slurry is then diluted by adding an amount of water corresponding to approximately 5-10

5. times the volume of the primary slurry. The final slurry is introduced into a Hatschek machine in which the solid material is picked up from a slurry bath by a rotary sieve cylinder which transfers the material to a continuously moving permeable belt, where the

10. material is further dewatered. Then the material is transferred as a thin layer onto a rotating cylinder, called the forming roll, and when a sufficient number of thin layers have been wound upon the forming roll, the material is removed as a green board capable of

15. being shaped and compressed before the curing.

20. 25.

Asbestos fibres possess special properties which make them suitable for these processes. Not only do they show good reinforcement properties in the final product, but also excellent properties during the sheet formation processes.

However, various limitations on the use of asbestos fibres have made it necessary to develop alternative fibre reinforced materials which can be produced on the machines used for the manufacture of

30. asbestos cement products, but reinforced with non

asbestos fibres. Various fibres, including glass fibres, steel fibres, and natural and synthetic organic fibres, have been suggested as replacement of asbestos fibres.

5. None of the experiments dealing with replacing asbestos fibres by only one other type of fibres, have however, been completely successful.

Considerable problems often arise during the production process, as it has been difficult to provide an approximately homogeneous distribution of the fibres in the slurry; both glass, cellulose and a number of plastic fibres show, for instance, a marked tendency to balling and lump formation instead of distributing themselves evenly in the slurry.

10. 15. The tendency to balling particularly grows with: decreasing W/S ratio, increasing fibre concentration and increasing length and elasticity of the fibres. By the Hatschek method a non-homogeneous fibre distribution may manifest itself in the final slurry

20. by formation of clouds exhibiting an increased density of fibres and binder particles. These clouds lead to problems during take up on the rotary sieve cylinder.

25. 30. Another problem arises during the dewatering where e.g. the glass fibres and most of the plastic fibres are incapable of retaining the binder particles which consequently are sucked away together with the water phase. These poor retention properties also manifest themselves by a non-homogeneous sheet structure, which by the Hatschek method may lead to

delamination of the green or cured sheets.

Poor retention both by the Magnani and by the Hatschek method further leads to loss of plasticity of the green sheets, whereby subsequent shaping is

5. impeded, and also to a tendency to moisture movements of the green sheets, which may lead to formation of micro cracks already during the curing.

Finally, the quality of the end product may be unsatisfactory. Glass fibre reinforced cement boards

10. may thus show fine initial strengths, but due to chemical decomposition of the glass fibres in the alkaline matrix the strength properties often drop catastrophically in short time. Cement boards reinforced with spun plastic fibres, e.g. of nylon or

15. polyolefine, often show poor strength, probably due to poor anchoring of the fibres in the matrix.

Inhomogeneous fibre distribution may result in fibres protruding through the surface of the sheets, causing reduced weathering and frost resistance properties.

20. It has been suggested to modify the essential properties of the slurry by addition of a number of additives including organic flocculants, dispersion agents, wetting agents, thickening agents and plasticifying agents.

25. By this certain problems may be eliminated, however often at the price of making other problems the more marked.

It is for example possible to provide an improved retention of binder particles by adding a flocculant to the slurry. In return fine continuous dewatering

channels may be formed in the final product, leading to reduced strength properties. E.g. GB application No. 2 035 285 suggests the use of a combination of finely divided siliceous materials having a small

5. particle size, preferably less than 10 micron, and a flocculant as a size coating on glass fibres and in a slurry of cement particles and glass fibres in order to produce high strength glass fibre reinforced cementitious products.

10. Addition of organic thickening and dispersion agents may affect the hardening properties of the hydraulic binder adversely, thus necessitating further addition of hardening accelerators, but as the process water, for environmental reasons, is recirculated, it is difficult to keep the concentrations of these additives at the desired values.

15. When comparing the properties of asbestos fibres with those of the proposed replacement fibres, it is seen that the properties of the asbestos fibres

20. are special in at least three respects: first of all the asbestos fibres have a specific surface area which is far larger than most types of replacement fibres. Secondly, the asbestos fibres exhibit a far larger variation in size than the replacement fibres.

25. Thirdly, the asbestos fibres have hydrophilic properties which by far exceed those of most of the suggested replacement fibres.

These properties probably all play a significant part for the easiness by which it is possible to

30. manufacture and handle the green asbestos cement sheets.

Consequently, it has been proposed to replace the asbestos fibres not by one but by two types of fibres, reinforcing fibres acting as reinforcing elements in the cured board, and retention fibres typically

5. having a length about one tenth the length of the reinforcing fibres and preferably being fibrillated and having a hydrophilic character.

Due to the large specific surface of the retention fibres a lattice structure is formed ensuring

10. an even distribution of the binder particles. During the suction of the excess water when manufacturing the green sheets this lattice structure acts as a filter, partly preventing the binder particles from being sucked away together with the water phase,
15. partly preventing the binder particles from being drawn away from the surface of the reinforcing fibres. Hydrophilic retention fibres furthermore ensure an appropriate retention of water in the green sheets.

DE OS 28 19 794 discloses for instance a process

20. for the manufacture of fibre reinforced shaped articles with cellulose fibres as retention fibres and a special type of polypropylene fibres as reinforcing fibres. However, when preparing as well a Magnani as a primary Hatschek slurry, problems may occur due to formation of lumps. By the Hatschek method further problems may arise due to formation of the above-mentioned clouds in the final slurry.
- 25.

These problems can be solved as described in Danish patent application No. 4926/78 by passing the

30. slurry through a high shear field in a narrow space

between two surfaces moving at high velocity relatively to each other. It is further mentioned that the incorporation of a fine filler such as silica dust consisting of spherical particles having a specific surface area about  $25 \text{ m}^2/\text{g}$  in the slurry improves the processability of the slurry.

As the high shear treatment is an energy consuming extra work operation causing heavy wear, and as the addition of the fine silica dust often causes problems of filtration in case of the Magnani method and poor retention in case of the Hatschek method, it is desirable to find other solutions to the lump formation problem.

In EP patent application No. 0 012 546 addition of ball clay to a slurry of cement particles, reinforcing and retention fibres is suggested as a means of reducing shrinkage of the green boards during curing of the cement.

However, the basic problem of avoiding the formation of fibre lumps in the slurry in a simple way and providing a slurry with excellent dewatering properties remains to be solved.

It has now surprisingly been found that this problem can be solved by a modified slurry preparation.

Hence, the present invention relates to a process for the manufacture of fibre reinforced shaped articles with a matrix of cured inorganic binder comprising the steps of

preparing an aqueous slurry of reinforcing fibres,

30. retention fibres, hydraulic inorganic binder par-

8.

ticles and possibly other additives and containing an excess of water in relation to the amount necessary to secure hydration of the inorganic binder,

5. forming green shaped articles by dewatering the slurry, and curing the green shaped articles, which is characterized in that the preparation of the aqueous slurry comprises the steps of initially preparing an aqueous pulp of reinforcing and retention fibres containing colloidal hydrophilic inorganic particles suspended in the water phase, and
10. subsequently forming the aqueous slurry by suspending the hydraulic inorganic binder particles and possibly other additives in said aqueous pulp, additional water being added, if desired.
15. Hydraulic inorganic binders include: Portland cement; Sorel cement; alumina cement; natural cement; cements containing granulated blast furnace slag, such as slag cement, Portland blast furnace cement and supersulphated cement; pozzolanic cements containing one of the above mentioned cements and/or lime and natural or artificial pozzolanas, such as kieselgur, trass, Santorin earth, fly ash and the
20. above mentioned silica dust; and gypsum plaster, in amounts of 98 to 60 % by weight calculated on total solid material.
25. Retention fibres include: refined cellulose fibres or synthetic organic fibres, such as highly fibrillated polyethylene or polypropylene fibres,
- 30.

such as Pulpex from Solvay et Cie. S.A., Ferlosa from Montedison, Carifil from Shell Chemicals and FPE from Schwarzwälder Textilwerke, preferably cellulose fibres refined to a fineness of 20-60 degrees on the

5. Schopper Riegler scale, added in amounts of 3-8 % by weight when using the Hatschek method and 0.25-4% by weight when using the Magnani method, in both cases calculated on total solid material.

10. Reinforcing fibres include: natural and synthetic organic or inorganic fibres, preferably added in an amount corresponding to 0.2-8 % by weight of solids in aqueous slurry.

15. Preferred natural organic reinforcing fibres are cellulose fibres, such as Kraft cellulose, hemp cellulose, abaca cellulose, cotton cellulose.

20. Preferred synthetic organic reinforcing fibres are polyamide, polyester and polyolefine fibres, in particular nylon 6, nylon 11, polyethylene and polypropylene fibres, especially chopped, fibrillated polypropylene fibres having a tensile strength of at least 4000 kp/cm<sup>2</sup> and an elongation at rupture of at most 8%, preferably chopped to a length of about 12 mm.

25. Preferred inorganic reinforcing fibres are glass fibres and stonewool fibres.

30. Preferred reinforcing fibres are cellulose fibres in amounts of 1-7% by weight and the above mentioned polypropylene fibres in amounts of 0.20 to 4% by weight, in both cases calculated on total solid material.

30. The preferred colloidal hydrophilic inorganic

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10. particles are those included in the group comprising:

- 1) hydrophilic silica particles with a specific surface above  $100 \text{ m}^2/\text{g}$  and preferably with an average particle diameter about 0.012 micron,
- 2) refined needle or plate shaped clay particles with a specific surface above 75  $\text{m}^2/\text{g}$  and preferably a thickness about 0.012 micron,
- 3) colloidal clay particles formed by suspending naturally occurring, preferentially sedimentary, clay in water, preferably in the presence of a clay dispersion agent, such as sodium hexametaphosphate, sodium pyrophosphate, water glass, sodium and potassium hydroxide and carbonate, preferably with a specific surface above 25  $\text{m}^2/\text{g}$ .

Preferred hydrophilic silica particles are commercially available as silica sols, such as Ludox<sup>R</sup> from du Pont, Syton<sup>R</sup> from Monsanto Co., Nalcoag<sup>R</sup> from Nalco Chem. Co., and Nyacol<sup>R</sup> from Nyanza Inc., and Davison Div., Grace Co., Santocel<sup>R</sup> from Cabot Corp., Syloid<sup>R</sup> from Vaylar<sup>R</sup> from PPG Industries, Aerosil<sup>R</sup> from Degussa Inc., and Quso<sup>R</sup> from Engelhard A.G.

Preferred refined needle or plate shaped clay particles are Attagel<sup>R</sup> a refined attapulgus clay product from Engelhard A.G.

The colloidal clay particles formed by suspending naturally occurring clay in water are preferentially used as aqueous suspensions of sedimentary clays, in

particular non kaolinitic clays, containing a clay dispersion agent and having a content of solid material about 40 % by weight.

The preferred amounts of added hydrophilic

5. silica are 0.5 to 8 % by weight, the preferred amounts of added refined needle or plate shaped clay particles are 0.5 to 2.5 % by weight and the preferred amounts of colloidal clay particles formed by suspension are 4 to 20 % by weight; in all cases calculated as solid material per total solid material.
- 10.

According to the invention a single member or a combination of members of the group may be added to the pulp as colloidal hydrophilic inorganic particles.

It is believed that the colloidal hydrophilic

15. inorganic particles defined above act as inorganic dispersion agents for the fibres, and it has been found that the two step preparation of the slurry comprising suspending the colloidal hydrophilic inorganic particles (in the following also named "the colloidal dispersion agent") in the water phase of the fibre pulp, i.e. preparing and using an aqueous colloidal solution as water phase in the fibre pulp or stock, in the first step is essential for achieving a satisfactory fibre dispersion in the slurry prepared in
- 20.
- 25.

the next step.

The order of mixing the components, i.e. water, retention and reinforcing fibres and colloidal

hydrophilic inorganic particles, in the pulp prepared in the first step of the preparation of the aqueous

30. slurry is not critical. However, an efficient dis-

persion of the colloidal particles into the water phase and a thorough mixing of fibres and the aqueous colloidal solution are important.

According to a preferred embodiment of the invention

5. the aqueous pulp of reinforcing and retention fibres containing colloidal hydrophilic inorganic particles suspended in the water phase is prepared as follows: a pulp of retention and reinforcing fibres in water is formed, then the colloidal hydrophilic
10. inorganic particles are added to the pulp and suspended into the water phase by stirring the pulp, and finally additional reinforcing fibres may be admixed into the pulp, if desired. The colloidal hydrophilic inorganic particles may be added to and suspended in
15. the water phase as a dry powder or as an aqueous suspension.

In some cases it may be desirable to improve the dewatering properties of the final aqueous slurry.

According to another aspect of the invention

20. this can be achieved by adding as an additive in the second step in the preparation of the aqueous slurry elongated inorganic particles with a length to diameter ratio larger than 3, preferably larger than 10, and preferably a diameter smaller than 0.1 mm, preferably stonewool fibres or acicular Wollastonite crystals.
- 25.

By this is obtained considerably improved filtering properties without the loss of strength accompanying addition of flocculants.

30. Additives added during the second step of the preparation of the aqueous slurry may further comprise

e.g. known fillers, colouring agents, setting and curing regulators and water-proofing agents.

When the green shaped articles are formed according to the Magnani technology, the aqueous

5. slurry, having a W/S-ratio equal to about 1, can be used immediately for the further handling in the Magnani machine. Due to a highly improved fibre distribution improved retaining properties of the retention fibres are observed. Further the excellent properties of the slurry with respect of distributing, carrying and supporting the fibres, in particular the reinforcing fibres, manifest themselves by fine surface character and high strength of the end product.
- 10.

15. When using the Hatschek technology, the primary aqueous slurry, having a W/S ratio equal to about 2, is diluted approximately 5 - 10 times with water.

20. Due to the improved dispersion of the fibres in particular of the reinforcing fibres an improved homogeneity of the slurry manifests itself by improved operating characteristics during the web forming process on the sieve cylinder, during the dewatering process and during the take up on the forming roll, resulting in an excellent end product.

25. The invention is further illustrated in the Examples:  
The materials used in the Examples were as follows:

Hydraulic inorganic binders.

Portland cement : Type I, specific surface  
(Blaine) about 3300 cm<sup>2</sup>/g

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14.

L.A. cement

: Low alkali portland cement,  
specific surface (Blaine)  
about 3000 cm<sup>2</sup>/g

E. cement

: A special coarse portland  
cement, specific surface  
(Blaine) about 2600 cm<sup>2</sup>/g

5.

Pozzolanic additives.

Silica dust

: Fine filter dust from  
electro-thermal production  
of Si, SiO<sub>2</sub>, content: 80-95%,  
specific surface: about  
25 m<sup>2</sup>/g, average particle  
diameter: about 0.1 micron

Fly ash

: Fly ash from power plant,  
specific surface: about  
3500 cm<sup>2</sup>/g

Filler.

ASP 400

: Hydrous aluminium silicate,  
flat plates, average par-  
ticle size: about 5 micron.

20.

Retention fibres.

B0 cellulose

: Bleached cellulose fibres  
(Betula) having a degree of  
freeness about 20 on the  
Schopper Riegler scale,  
length: about 1.3 mm,  
diameter: about 30 micron.

E0 cellulose

: Bleached cellulose fibres  
(Myrtaceae) having a degree  
of freeness about 20 on the  
Schopper Riegler scale,  
length: about 1.0 mm, dia-  
meter: about 20 micron.

25.

30.

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Reinforcing fibres.

A0 cellulose : Cellulose fibres (*Pinus*)  
(*Kraft cellulose*), length:  
less than 4 mm, diameter:  
about 35 micron. These  
fibres comprise a fine  
fraction acting as reten-  
tion fibres.

5. Abaca : Cellulose fibres (*Musa*),  
length: about 6 mm, dia-  
meter: about 30 micron

10. Cotton : Chopped cellulose fibres  
(*Gossypium*), length: about  
10 mm, diameter: about 10-  
20 micron. These fibres  
comprise a fine fraction  
acting as retention fibres.

15. CEMFIL : Bundles of alkali-resistant  
glass fibres from Fiber-  
glass Ltd., length about 10  
mm, filament diameter about  
10 micron.

20. Polypropylene : Fibres prepared as de-  
scribed in Example 10.

25. Colloidal dispersion agents.  
Attagel<sup>R</sup> 150 : A commercial colloidal,  
acicular attapulgus clay  
product, specific surface:  
 $210 \text{ m}^2/\text{g}$

30.

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16.

Aerosil<sup>R</sup> 200

: Commercial alkali stabilized colloidal silica,  
specific surface 200 m<sup>2</sup>/g,  
average particle diameter:  
0.012 micron

Ludox<sup>R</sup> HS40

: Commercial alkali stabilized sili sol, silica  
content: 40%, specific  
surface: 220-235 m<sup>2</sup>/g,  
average particle diameter  
0.014 micron

10.

Clay slip Rørdal and Danmark: Colloidal watery slurries  
prepared from non refined  
sedimentary glacial clays,  
specific surface: 25 m<sup>2</sup>/g,  
40 % by weight solid  
material.

15.

Filtering aids.

NYAD<sup>R</sup> G

20.

: Acicular Wollastonite  
crystals, length: about 22  
micron, length t diameter  
ratio: 5-15.

Stonewool fibres

: Commercial stonewool fibres  
(from Conrock) length: about  
0.75 mm, diameter: 5 micron

25.

? Fibre reinforced sheets were prepared in the  
laboratory in bench scale, on a Magnani machine in full  
industrial scale, and on a Hatschek machine in full  
30. industrial scale:

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Bench scale experiments:Production procedure A.

Pulp preparation: A solution was prepared of 3.4 g Ca(OH)<sub>2</sub> and 5.1 g CaSO<sub>4</sub>, 2H<sub>2</sub>O in 1700 ml deionized

5. water. The solution was introduced into a British Pulp Evaluation Apparatus. About 80 g retention and reinforcing fibres, apart from polypropylene fibres, were added to the solution, and the mixture was pulped for 15 minutes at 3000 r.p.m. When desired, about 4 g
10. polypropylene fibres were then added, and the resulting mixture pulped for 2.5 minutes.

Slurry preparation: The resulting fibre pulp was transferred to a vessel and a slurry was prepared by adding hydraulic inorganic binder and optionally pozzolanic

15. and other additives to the stirred pulp (285 r.p.m.) in an amount corresponding to 1700 g total solid material. The slurry was stirred for 3 minutes.

Preparation of green sheets: A portion of slurry corresponding to 140 g solid material was pressed to

20. green sheets in a Johns-Manville sheet forming press at 15 kp/cm<sup>2</sup> for 60 seconds.

Preparation of hardened sheets: The green sheets were cured to hardened sheets in the following way: The green sheets were placed on a glass plate and kept in a humidity box for 24 hours, relative humidity: about 95%, temperature 25°C. Thereafter the sheets were submerged in water for 6 x 24 hours, temperature: 25°C.

25. 30. This procedure was used when producing a slurry having a weight ratio water/total solid material equal to about 1, corresponding to the ratio used in the

Magnani method. In order to investigate the properties of a Hatschek slurry having a corresponding ratio equal to 10, the following procedure was used:  
Production procedure B.

5. Pulp preparation: A pulp comprising about 20 g fibres in 2000 ml of the above-mentioned solution was prepared as described in production procedure A.

10. Slurry preparation: The fibre pulp was transferred into the vessel of a Diaf mixer, and an additional amount of the above-mentioned solution was added to a total volume of water equal to 5000 ml. The resulting mixture was stirred at 4000 r.p.m., and a slurry was prepared by adding hydraulic binder and optionally pozzolanic and other additives to the stirred pulp in an amount corresponding to 500 g total solid material. The slurry was stirred for 6 minutes.

15. Preparation of green sheets: 1300 ml portions of the slurry were dewatered in a filtering apparatus, suction pressure 200 mm Hg. The resulting filter cakes were pressed to green sheets in a Johns-Manville sheet forming press at 15 kp/cm<sup>2</sup> for 60 seconds.

20. Preparation of hardened sheets: As described in production procedure A.

25. A number of products were prepared according to the invention (type of experiment I) and a number was prepared for comparison (type of experiment C).

30. When products were prepared according to the invention, the colloidal dispersion agent was added during the pulp preparation phase before the addition of polypropylene fibres, and the pulp was stirred for

2.5 minutes after the addition of colloidal dispersion agent.

The physical properties of the slurry and the hardened sheets were measured and estimated as described below:

Testing procedures:

Filtration time: Slurry preparation according to production procedure A: A portion of slurry corresponding to 180 g of solid material was dewatered in

10. a filtration apparatus at a suction pressure equal to 200 mm Hg. A sudden drop in suction pressure indicates the end of the filtration period. The filtration time is defined as the period of time from start of suction to pressure drop.

15. Slurry prepared according to procedure B: Same procedure as above, but using 1300 ml of slurry.

Loss of solids: The particle retention properties of the slurry prepared according to production procedure B were measured in the following way. 3 times 440 g portions of slurry were dewatered in a filtration apparatus provided with a 40 mesh sieve, suction pressure: 30 mm Hg. The content of solid material in the filtrate was filtered out from the filtrate and the weight thereof determined. Loss of solids is defined as the percentage by weight of solid material in filtrate compared to total amount of solids.

Character of slurry: The tendency of the fibres to ball and form lumps in the slurry prepared according to production procedure A was estimated manually by rubbing the slurry between the fingers. The properties

of the slurry were given the following Characters:

"1": Smooth slurry with no lumps.

"2": Small lumps present.

"3": Big lumps present.

5. BT-max dry and wet, 7 days: The hardened sheets were subjected to bending tests in which the curvature of the specimens was determined as a function of the load. A ZWICK 1474 testing machine with 4-point load with a support distance of 190 mm and a 35 mm arm of momentum was used. Force/deformation curves were registered. BT-max designates the maximum tensile stress in bending at maximum load. Subscript "wet" designates that the sheets were taken directly from the hardening phase, "dry" designates that the fresh hardened sheets were dried for 48 hours at  $110^{\circ}\text{C}$  before they were subjected to bending test.

Example 1.

Comparison of sheets prepared according to the invention and sheets prepared according to the known art.

20. (Production procedure A.)  
7 series of experiments were performed with production of sheets according to production procedure A.

In experiments 1 and 5 sheets were produced without addition of any colloidal dispersion agent.

In experiments 2-4 and 6-7 colloidal dispersion agents were added to the fibre pulp according to the invention as described above.

Compositions and test results appear from table I.  
30. It is evident that the sheets prepared according

to the invention are superior to the sheets prepared for comparison.

5. The production of the sheets in experiment 5 was extremely difficult due to extreme tendency to fibre balling. Therefore it was necessary to operate at a rather high W/S ratio. These problems were completely absent in experiments 6 and 7.

Example 2.

Effect of incorporating Wollastonite crystals.

10. 3 series of experiments were performed with production of sheets according to production procedure A including addition of NYAD G to the slurry. Compositions and test results appear from table II.

15. Comparison between the results of experiments 2 and 8, 3 and 9, and 4 and 10 shows that incorporating NYAD G provides reduced time of filtration and improved strength. Preferred values for the filtration time are 15-50 seconds. Values below 15 seconds indicate too rapid dewatering due to formation of a porous structure in the matrix, leading to weak hardened sheets. Values above 50 seconds are not desirable - because they lead to reduced production capacity.

Example 3.

25. Effect of adding colloidal dispersion agent to the fibre pulp compared to adding some material to the slurry.

Six series of experiments were carried out with production of sheets according to production procedure A.

30. In three series (example 11, 13 and 15) the

colloidal dispersion agent was added to the fibre pulp, i.e. according to the invention. In the other three series (example 12, 14 and 16) the colloidal dispersion agent was not added according to the

5. invention, i.e. not to the fibre pulp, but to the slurry.

Compositions and test results appear from table III.

10. It is evident that the order of mixing the components is essential for obtaining a superior product.

Example 4.

Production of sheets according to the invention.

15. 12 series of experiments were performed with production of sheets according to production procedure A with different combinations of colloidal dispersion agent added to the fibre pulp. Experiments 29-32 show the effect of not including any colloidal dispersion agent.

20. Compositions and test results appear from Table IV.

The superiority of the sheets prepared according to the invention is evident.

Example 5.

Effect of addition of a flocculating agent.

25. It was shown in example 2 that the incorporation of Wollastonite crystals resulted in improved strength and reduced filtration times.

30. Reducing filtration time by addition of flocculating agents, such as cationic polyelectrolytes, belongs to the known art. The effect of addition of flocculation

agents was investigated in the following way.

Two series of experiments were performed with production of sheets according to production procedure A. In both series 20% by weight (on dry basis) clay

5. slip Rørdal was added to the fibre pulp according to the invention, but in experiment 34 0.025% by weight of a strongly cationic polyacrylamide polyelectrolyte "X 1" from Floerger S.A. was added to the slurry as flocculating agent.

10. Compositions and test results appear from table V.

The addition of flocculating agent resulted in a reduced filtration time but also in reduced strength. Addition of Wollastonite crystals results in reduced filtration time and improved strength.

15. Example 6.

Effect of addition of fine silica dust.

Addition of fine silica dust, i.e. silica dust as defined above, to the slurry belongs to the known art. The essential difference between silica dust

20. and the colloidal hydrophilic inorganic particles according to the invention was illustrated through the following experiments with production of sheets according to production procedure A.

25. In the first experiment, experiment No. 35, 2 weight % silica dust was mixed into the fibre pulp, in the second experiment, No. 36, 2 weight % Attagel 150 was mixed into the fibre pulp, in the third experiment, No. 37, 2 weight % Attagel 150 was mixed into the fibre pulp, and 2 weight % silica dust was added to the slurry, and in the fourth experiment, No. 38,
- 30.

neither silica dust nor Attagel 150 was added, neither to pulp nor slurry.

Compositions and test results appear from table VI.

5. The results demonstrate that addition of silica dust to the pulp does not prevent lump formation in the slurry as Attagel 150 does. Comparison between experiments 35 and 38 shows a minor increase of BT-max, dry by addition of silica dust, which may be explained  
10. by the excellent pozzolanic activity of the silica dust.

It is obvious that the products prepared according to the invention are superior with respect to strength properties. Also the surface character  
15. of the products prepared according to the invention is better, because the sheets prepared in experiments 36 and 37 have a smooth surface, whereas the surface of the sheets prepared in experiments 35 and 38 exhibit protruding fibres.

20. The sheet prepared in experiment 36 is preferred to the sheet prepared in experiment 37 because addition of a small amount of silica dust, even less than 1 % by weight, causes an undesirable dark colouring of the sheets.

25. Example 7.

Comparison of sheets prepared according to the invention and sheets prepared according to the known art.  
(Production procedure B).

30. 12 series of experiments were performed with production of sheets according to production procedure B.

The B0 cellulose fibres were refined to a degree of freeness about 58 on the Schopper Riegler scale after pulping.

5. In three experiments (experiment 39, 45 and 49) sheets were produced without addition of any colloidal dispersion agents.

In other experiments colloidal dispersion agent was added to the fibre pulp as described above.

10. Experiments 44 and 48 illustrate the effect of adding NYAD G and stonewool fibres to the slurry.

Compositions and test results appear from table VII.

15. The results demonstrate that a significant increase of the strength of the sheets is achieved by the addition of colloidal dispersion agent to the fibre pulp.

A filtration time below 300 seconds is preferred, and a loss of solids about 10% is acceptable by the mentioned production procedure.

20. Experiments 47-48 show the efficiency of NYAD G as filtration aid.

Example 8.

Experiments on a full scale Magnani machine.

25. 146 kg A0 cellulose and 122 kg B0 cellulose were pulped with 6500 litres of water for 40 minutes in a 12 m<sup>3</sup> Black Clawson pulper. Thereafter 24 kg of polypropylene fibres were added, and the pulp was pulped for 5 minutes. Then 122 kg Attagel 150 was added, and the mixture was pulped for 10 minutes.

30. Finally, an amount of clay slip Rørdal corresponding

to 974 kg dry material was added and the pulp was pulped for 5 minutes.

The pulp was transferred to a 4 m<sup>3</sup> F. L. Smidth mixer and portland cement, NYAD G and Wollastonite FW200 (Wollastonite particles with average length about 20 micron, length to diameter ratio about 3 from Pargas Kalk AB) was added in amounts corresponding to 80 kg portland cement, 10.2 kg NYAD G and 6.8 kg Wollastonite FW200 per 107 kg pulp. The resulting slurry was stirred for 15 minutes. Then the slurry was pumped into a Magnani machine where it was dewatered to corrugated boards.

The boards were stacked and conveyed through a curing channel where they were cured by the heat developed by the hydration of the cement. The residence time in the curing channel was about 7 hours. After about 4 hours a temperature of 100°C was reached. The cured boards were removed from the forms and stored at 25°C for 7 days.

20. Testing.

The BT-max of the boards was measured essentially as described above, but with 3-point load.  
BT-max l (with rupture parallel to the corrugations)  
8.1 MPa.  
BT-max t (with rupture perpendicular to the corrugations)  
9.3 MPa Density: 1.45 g per cm<sup>3</sup>.

Example 9.

Experiments on a full scale Hatschek machine.

Experiment H1.

30. 86 kg abaca cellulose was pulped for 30 minutes

with 2500 litres of water in a 3 m<sup>3</sup> Solvo pulper.  
138 kg B0 cellulose was pulped for 10 minutes with  
4000 litres of water in a 7 m<sup>3</sup> Solvo pulper. The  
resulting B0 cellulose pulp was refined to 50.

5. degrees of fineness on the Schopper Riegler scale.  
The two pulps were transferred to a 7 m<sup>3</sup> Solvo pulper  
and 68 kg Attagel 150 was mixed into the pulp.  
Mixing time: 5 minutes. Then an amount of clay slip  
Rördal corresponding to 512 kg solid material, 171 kg  
10. stonewool fibres and 17 kg polypropylene fibres  
were added, and the mixture was mixed for 10 minutes.  
3383 kg of the resulting pulp was mixed with  
99<sup>1/4</sup> kg E. cement to a primary Hatschek slurry with  
a W/S ratio, i.e. a ratio water to total solid  
15. material, equal to about 2.1.

The primary slurry was diluted with water to a  
W/S ratio equal to about 10, and processed into plane  
boards by known methods in a Hatschek machine. The  
boards were pressed at 125 kp/cm<sup>2</sup> for 20 minutes,  
20. and the pressed boards were cured and stored for 28  
days as described in example 8.

Testing.

Two values of BT-max of the boards was measured  
as described in connection with the bench scale  
25. experiments.

BT-max l (with rupture parallel to the direction of  
the permeable belt).

BT-max t (with rupture perpendicular to the direction  
of the permeable belt).

30. Composition and test results appear from table VIII.

Experiments H2-H5

Four other types of boards were produced as described above.

Compositions and test results appear from  
5. table VIII.

Example 10.Preparation of the polypropylene fibres used in Examples 1-9.

The fibres were prepared in the following manner:

10. The polypropylene used was GWE 23 from ICI with melt index of 3 g/10 minutes measured according to DIN MFI 230/2.16.

15. In a standard extrusion/stretch plant, the polypropylene was extruded into a blown tubular film at an extruder temperature of 180-220°C, and the tubular film was cooled with cooling air at 18-20°C and cut into two film bands.

20. From the drawing station following the extruder, the film was passed through a hot air oven with an air temperature of 180°C and an air velocity of 25 m/second. By using a higher roller speed in the stretch station following the hot air oven, the film was stretched in a ratio of 1:17. Thereafter, the film was heat-stabilized by passing a hot air oven with an air temperature of 180°C and an air velocity of 25m/second, the film velocity being about 90 m/second.

25. The thickness of the film was then 20 micron.  
The film was fibrillated to form fibres of from 2 to 30 dtex by means of a Reichenhäuser FI-S-0800-03-01 fibrillator with 13 needles per cm in each of two

consecutive staggered needle rows placed with the same distance as the interval between two needles.

5. The fibrillation ratio (=the ratio between the film advancing velocity and the circumferential velocity of the fibrillator roll) was 1:3. Thereafter, 1% by weight of hydrophilic avivage (Henkel LW 421) was applied as an 1:9 aqueous slurry, and the fibres were cut in lengths of 12 mm in a staple cutter.

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30.

TABLE I

Experiment No.	1	2	3	4	5	6	7
	(% by weight, dry basis)						

<u>Portland Cement</u>							
<u>L.A. Cement</u>							
<u>E. cement</u>	97.75	95.75	95.75	95.75	94.5	74.5	90.75
<u>Silica dust</u>							
<u>Fly ash</u>							
<u>B0 cellulose</u>							
<u>E0 cellulose</u>							
<u>A0 cellulose</u>	2.0	2.0	2.0	2.0	5.0	5.0	5.0
<u>Abaca</u>							
<u>Cotton</u>							
<u>Polypropylene</u>	0.25	0.25	0.25	0.25	0.25	0.25	0.25
<u>Attagel 150</u>					2.0		4.0
<u>Aerosil 200</u>			2.0				
<u>Ludox HS 40</u>				2.0			
<u>Clay slip Rørdal</u>							
<u>Clay slip Danmark</u>						20	
<u>NYAD G</u>							
<u>Stonewool fibres</u>							
<u>TYPE OF EXPERIMENT</u>	C	I	I	I	C	I	I
<u>W/S in slurry (x)</u>	1.0	1.0	1.0	1.0	1.3	1.05	1.3
<u>Filtration time (sec.)</u>	17	100	61	31	9	57	28
<u>Density, g/cm<sup>3</sup></u>	1.65	1.74	1.75	1.72	1.42	1.63	1.52
<u>BT-max wet, 7 days, MPa</u>	7.3	8.6	8.3	9.4	6.6	13.2	10.7
<u>BT-max dry, 7 days, MPa (y)</u>	(y)	(y)	(y)	(y)	8.8	15.1	11.3
<u>Character of slurry</u>	3	1	1	1	3	1	1

(x) weight ratio water/total solid material

(y) not measured

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31.

TABLE II

Experiment No.

8      9      10

(% by weight, dry basis)

<u>Portland cement</u>			
L.A. cement			
<u>E. cement</u>	83.75	83.75	83.75
Silica dust			
<u>Fly ash</u>			
B0 cellulose			
<u>E0 cellulose</u>			
A0 cellulose	2.0	2.0	2.0
Abaca			
Cotton			
<u>Polypropylene</u>	0.25	0.25	0.25
Attagel 150			2.0
Aerosil 200	2.0		
Ludox HS 40		2.0	
Clay slip Rørdal			
Clay slip Danmark			
NYAD G	12.0	12.0	12.0
<u>Stonewool fibres</u>			
 TYPE OF EXPERIMENT	I	I	I
 <u>W/S in slurry (x)</u>	1.0	1.0	1.0
<u>Filtration time (sec.)</u>	29	30	15
<u>Density, g/cm<sup>3</sup></u>	1.54	1.61	1.65
<u>BT-max wet, 7 days, MPa</u>	10.6	10.9	10.6
<u>BT-max dry, 7 days, MPa</u>			
<u>Character of slurry</u>	1	1	1

(x) weight ratio water/total solid material

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32.

TABLE III

Experiment No.	11	12	13	14	15	16
----------------	----	----	----	----	----	----

(% by weight, dry basis)

<u>Portland cement</u>						
<u>L.A. cement</u>						
<u>E. cement</u>	87.25	87.25	73.75	73.75	92.5	92.5
<u>Silica dust</u>						
<u>Fly ash</u>						
<u>B0 cellulose</u>	1.5	1.5			0.5	1.5
<u>E0 cellulose</u>						
<u>A0 cellulose</u>	2.0	2.0	2.0	2.0		
<u>Abaca</u>						
<u>Cotton</u>						
<u>Polypropylene</u>	0.25	0.25	0.25	0.25	3.0	3.0
<u>Attagel 150</u>	2.0	2.0				
<u>Aerosil 200</u>					3.0	3.0
<u>Luciox HS E.C.</u>						
<u>Clay slip Rördal</u>	7.0	7.0				
<u>Clay slip Danmark</u>			12	12		
<u>NYAD G</u>			12	12		
<u>Stonewool fibres</u>						
 TYPE OF EXPERIMENT	I	C	I	C	I	C
 <u>W/S in slurry (x)</u>	1.0	1.0	0.85	0.85	0.9	0.9
<u>Filtration time (sec.)</u>	48	29	49	20	45	18
<u>Density, g/cm<sup>3</sup></u>	1.58	1.48	1.66	1.53	1.62	1.36
<u>BT-max wet, 7 days, MPa</u>	10.4	6.6	12.4	6.2	12.8	5.8
<u>BT-max dry, 7 days, MPa</u>						
<u>Character of slurry</u>	1	3	1	3	1	3

(x) weight ratio water/total solid material

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34.

TABLE IV (continued)

Experiment No.	23	24	25	26	27	28
	(% by weight, dry basis)					
Portland cement	82.5					
L.A. cement		84.25	72.25	84.5		77.5
E. cement					77.75	
Silica dust			12.0	5.0		5.0
Fly ash						
B0 cellulose						
E0 cellulose	1.0	1.5	2.5	1.5		1.5
A0 cellulose	1.0			1.0	3.0	
Abaca						
Cotton		1.0				
Cemfil						5.0
Polypropylene	0.25	3.0	3.0	3.0	0.25	
Attagel 150	1.25	1.25	1.25		2.0	1.0
Aerosil 200						
Ludox HS 40						
Clay slip Rördal	7.0	10.0	10.0	10.0	5.0	10.0
Clay slip Danmark						
NYAD G		6.0			12.0	
Stonewool fibres						
TYPE OF EXPERIMENT	I	I	I	I	I	I
W/S in slurry (x)	1.0	1.0	1.0	0.9	1.0	0.8
Filtration time (sec.)	33	70	265	60	15	110
Density, g/cm <sup>3</sup>	1.65	1.62	1.63	1.49	1.56	1.77
BT-max wet, 7 days, MPa	12.3	13.2	15.4	10.2	11.4	16.7
BT-max dry, 7 days, MPa	13.3	17.2	17.5	12.6	11.6	17.8
Character of slurry	1	1	1	1	1	1

(x) weight ratio water/total solid material

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TABLE IV

Experiment No.	17	18	19	20	21	22
	(% by weight, dry basis)					

<u>Portland cement</u>						
L.A. cement				70.25	85.5	84.5
E. cement	77.5	89.75	83.5			
<u>Silica dust</u>						
<u>Fly ash</u>						
B0 cellulose		1.50	1.50			
E0 cellulose				1.5	1.5	
A0 cellulose	2.0	1.5	1.5			
Abaca						
Cotton				6.0		
Polypropylene	0.25	0.25	0.25	0.25	3.0	4.0
Attagel 150		1.25	1.25	3.5		
Aerosil 200						
Ludox HS 40						
Clay slip Rørdal				20.0	10.0	10.0
Clay slip Danmark	8.0	6.0	6.0			
NYAD G	12.0		6.0			
<u>Stonewool fibres</u>						
TYPE OF EXPERIMENT	I	I	I	I	I	I
W/S in slurry (x)	0.88	1.0	1.0	1.5	0.9	0.9
Filtration time (sec.)	18	68	32	86	88	68
Density, g/cm <sup>3</sup>	1.64	1.66	1.69	1.49	1.54	1.48
BT-max wet, 7 days, MPa	13.2	9.6	11.7	10.5	10.6	10.7
BT-max dry, 7 days, MPa	14.8	(y)	15.4	16.5	13.6	15.1
Character of slurry	1	1	1	1	1	1

(x) weight ratio water/total solid material

(y) not measured

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35.

TABLE IV (continued)

Experiment No.	29	30	31	32
	(% by weight, dry basis)			

<u>Portland cement</u>				
<u>L.A. cement</u>				
<u>E. cement</u>	74.75	94.75	94.75	97.0
<u>Silica dust</u>				
ASP 400	10.0			
<u>Fly ash</u>				
<u>B0 cellulose</u>			4.5	1.25
<u>E0 cellulose</u>	1.5	4.5		
<u>A0 cellulose</u>	1.5	0.5	0.5	1.5
<u>Abaca</u>				
<u>Cotton</u>				
<u>Polypropylene</u>	0.25	0.25	0.25	0.25
<u>Attagel 150</u>				
<u>Aerosil 200</u>				
<u>Ludox HS 40</u>				
<u>Clay slip Rørdal</u>				
<u>Clay slip Denmark</u>				
<u>NYAD G</u>	12.0			
<u>Stonewool fibres</u>				

TYPE OF EXPERIMENT	C	C	C	C
<u>W/S in slurry (x)</u>	0.9	1.2	1.2	1.0
<u>Filtration time (sec.)</u>	8	6	5	7
<u>Density, g/cm<sup>3</sup></u>	1.52	1.45	1.45	1.58
<u>BT-max wet, 7 days, MPa</u>	7.2	5.8	4.9	5.4
<u>BT-max dry, 7 days, MPa</u>	8.5	8.4	7.1	7.6
<u>Character of slurry</u>	3	3	3	3

(x) weight ratio water/total solid material

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36.

TABLE V

Experiment No.	33	34
	(% by weight, dry basis)	

<u>Portland cement</u>		
L.A. cement		
<u>E. cement</u>	74.75	74.75
Silica dust		
Fly ash		
B0 cellulose		
<u>E0 cellulose</u>		
A0 cellulose	5.0	5.0
Abaca		
Cotton		
<u>Polypropylene</u>	0.25	0.25
Attagel 150		
Aerosil 200		
Ludox HS 40		
Clay slip Rørdal	20.0	20.0
Clay slip Danmark		
NYAD G		
Cationic polyelectrolyte "X 1"	-	0.025

TYPE OF EXPERIMENT	I	I
--------------------	---	---

<u>W/S in slurry (x)</u>	1.2	1.2
Filtration time (sec.)	49	28
Density, g/cm <sup>3</sup>	1.63	1.57
BT-max wet, 7 days, MPa	10.2	7.6
BT-max dry, 7 days, MPa		
Character of slurry	1	2

(x) weight ratio water/total solid material

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37.

TABLE VI

Experiment No.	35	35	37	38
	(% by weight, dry basis)			

<u>Portland cement</u>				
<u>L.A. cement</u>				
<u>E. cement</u>	94.25	94.25	92.25	96.25
<u>Silica dust</u>	2.0		2.0	
<u>Fly ash</u>				
<u>B0 cellulose</u>	1.5	1.5	1.5	1.5
<u>E0 cellulose</u>				
<u>A0 cellulose</u>	2.0	2.0	2.0	2.0
<u>Abaca</u>				
<u>Cotton</u>				
<u>Cemfil</u>				
<u>Polypropylene</u>	0.25	0.25	0.25	0.25
<u>Attigel 150</u>		2.0	2.0	
<u>Aerosil 200</u>				
<u>Ludox HS 40</u>				
<u>Clay slip Rørdal</u>				
<u>Clay slip Danmark</u>				
<u>NYAD G</u>				
<u>Stonewool fibres</u>				
 <u>TYPE OF EXPERIMENT</u>	 C	 I	 I	 C
<u>W/S in slurry (x)</u>	1.0	1.0	1.0	1.0
<u>Filtration time (sec.)</u>	17	25	23	9
<u>Density, g/cm<sup>3</sup></u>	1.52	1.64	1.63	1.46
<u>BT-max wet, 7 days, MPa</u>	7.2	9.0	9.0	6.9
<u>BT-max dry, 7 days, MPa</u>				
<u>Character of slurry</u>	3	1	1	3

(x) weight ratio water/total solid material

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38.

TABLE VII

Experiment No.	39	40	41	42	43	44
(% by weight, dry basis)						
Portland cement						
L.A. cement						
E. cement	94.5	92.5	78.5	79.5	78.0	71.0
Silica dust						
Fly ash						
BO cellulose	4.5	4.5	4.5	4.5	4.0	4.0
EO cellulose						
AO cellulose	0.5	0.5	0.5	0.5		
Abaca					2.5	2.5
Cotton						
Polypropylene	0.5	0.5	0.5	0.5	0.5	0.5
Attagel 150			2.0			2.0
Aerosil 200						
Ludox HS 40				1.0		
Clay slip Rørdal				15.0	15.0	15.0
Clay slip Danmark						
NYAD G						
Stonewool fibres						5.0
TYPE OF EXPERIMENT	C	I	I	I	I	I
W/S in slurry (x)	10	10	10	10	10	10
Filtration time (sec.)	48	64	441	331	146	145
Loss of solids (%) (xx)	6.5	7.6	6.8	7.0	6.9	4.8
Density, g/cm <sup>3</sup>	1.42	1.44	1.57	1.55	1.48	1.36
BT-max wet, 7 days, MPa	5.4	7.0	11.5	10.7	11.2	9.5

(x) weight ratio water/total solid material

(xx) by weight

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39.

TABLE VII (continued)

Experiment No.	45	46	47	48	49	50
	(% by weight, dry basis)					

<u>Portland cement</u>						
<u>L.A. cement</u>						
<u>E. cement</u>	96.0	94	86	76	84.5	69.5
<u>Silica dust</u>						
<u>Fly ash</u>					10	10
<u>B0 cellulose</u>	3.0	3.0	3.0	3.0	4.5	4.5
<u>E0 cellulose</u>						
<u>A0 cellulose</u>	0.5	0.5	0.5	0.5	0.5	0.5
<u>Abaca</u>						
<u>Cotton</u>						
<u>Polypropylene</u>	0.5	0.5	0.5	0.5	0.5	0.5
<u>Attagel 150</u>		2	2	2		
<u>Aerosil 200</u>						
<u>Ludox HS 40</u>						
<u>Clay slip Rørdal</u>				6	8	
<u>Clay slip Danmark</u>						15
<u>NYAD G</u>					10	
<u>Stonewool fibres</u>						

TYPE OF EXPERIMENT	C	I	I	I	C	I
<u>W/S in slurry (x)</u>	10	10	10	10	10	10
<u>Filtration time (sec.)</u>	60	93	353	189	48	371
<u>Loss of solids (%) (xx)</u>	9.1	10.4	11.2	8.3	5.3	8.7
<u>Density, g/cm<sup>3</sup></u>	1.48	1.52	1.60	1.50	1.34	1.52
<u>BT-max wet, 7 days, MPa</u>	5.5	7.4	8.7	8.0	3.8	9.5

(x) weight ratio water/total solid material

(xx) by weight

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TABLE VIII

Experiment No.                    H1     H2     H3     H4     H5  
                                       (% by weight, dry basis)

<u>Portland cement</u>					
L.A. cement					
E. cement	71	86	76	79.5	69.5
Silica dust					
Fly ash					
BO cellulose SR50	4	4	4	4.5	4.5
EO cellulose					
AO cellulose				0.5	0.5
Abac	2.5	2.5	2.5		
Cotton					
Polypropylene	0.5	0.5	0.5	0.5	0.5
Attacel 150	2	2	2		
Aerosil 200					
Luc HS 40					
Clay slip Rørdal	15		15	15	15
Clay slip Danmark					10
NY G					
Stonewool fibres	5	5			
<u>TYPE OF EXPERIMENT</u>	I	I	I	I	I
<u>Density, g/cm<sup>3</sup></u>	1.63	1.63	1.46	1.49	1.70
BT-max l, 28 days, MPa	19.2	14.2	11.0	12.6	15.1
BT-max t, 28 days, MPa	26.2	18.8	17.1	19.0	18.2

BAD ORIGINAL

CLAIMS

1. A process for the manufacture of fibre reinforced shaped articles with a matrix of cured inorganic binder comprising the steps of preparing an aqueous slurry of reinforcing fibres, retention fibres, hydraulic inorganic binder particles and possibly other additives and containing an excess of water in relation to the amount necessary to secure hydration of the inorganic binder, forming green shaped articles by dewatering the slurry, and curing the green shaped articles, characterized in that the preparation of the aqueous slurry comprises the steps of initially preparing an aqueous pulp of reinforcing and retention fibres containing colloidal hydrophilic inorganic particles suspended in the water phase, and subsequently forming the aqueous slurry by suspending the hydraulic inorganic binder particles and possibly other additives in said aqueous pulp, additional water being added, if desired.

2. A process according to Claim 1, characterized in that the colloidal hydrophilic inorganic particles are selected from the group comprising

- 1) hydrophilic silica particles with a specific surface above  $100 \text{ m}^2/\text{g}$  and an average particle diameter about 0.012 micron,

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- 2) refined needle or plate shaped clay particles with a specific surface above  $75 \text{ m}^2/\text{g}$  and thickness about 0.012 micron,
- 3) colloidal clay particles formed by suspending naturally occurring, preferentially sedimentary, clay in water, preferably in the presence of a clay dispersion agent, with a specific surface above  $25 \text{ m}^2/\text{g}$ .

3. A process according to Claim 1 or Claim 2, characterized in that the reinforcing fibres are selected from the group comprising cellulose, polyamide, polyester and polypropylene fibres and added in an amount corresponding to 0.2-8% by weight of solids in the aqueous slurry.

4. A process according to any of Claims 1 to 3, characterized in that the reinforcing fibres comprise fibrillated polypropylene fibres having a tensile strength of at least  $4000 \text{ kp/cm}^2$  and an elongation at rupture of at most 8 %, chopped to a length of about 12 mm.

5. A process according to any of Claims 1 to 4, characterized in that the retention fibres are selected from the group comprising refined cellulose fibres, in particular cellulose fibres refined to a fineness of 20-60 degrees on the Schopper Riegler scale, and highly fibrillated polyethylene and polypropylene fibres, and added in an amount corresponding to 0.2-8 % by weight of solids in the aqueous slurry.

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6. A process according to any of Claims 1 to 5, characterized in that the first step in the preparation of the aqueous slurry comprises preparation of an aqueous pulp of retention and reinforcing fibres, followed by addition of colloidal hydrophilic inorganic particles to the pulp, mixing and suspending the particles into the water phase, if desired followed by addition of additional reinforcing fibres and further mixing.

7. A process according to any of Claims 1 to 6, characterized in that the colloidal hydrophilic inorganic particles are added to and suspended in the water phase of the pulp as an aqueous suspension.

8. A process according to any of Claims 1 to 7, characterized in that the second step in the preparation of the aqueous slurry comprises admixing elongated inorganic particles with a length to diameter ratio larger than 3, preferably larger than 10, and a diameter smaller than 0.1 mm, preferably stonewool fibres or acicular Wolastonite crystals.

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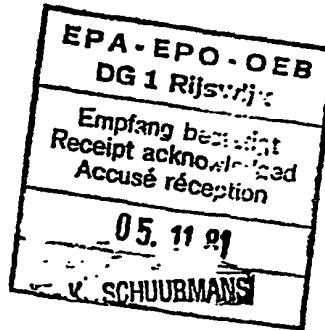
Telegrams and Cables:  
Bedkil, London WC1

Address for  
European Patent Office  
representation:  
(By appointment)  
8 Munich 40  
Röntgenstr. 24  
West Germany

Our Ref: AJMR/SH/SMIDTH 8540-1  
Your Ref:

Date: November 3, 1981

European Patent Office,  
Receiving Section,  
P.B. 5815 Patentiaan 2,  
2280 HV Rijswijk (ZH),  
THE HAGUE,  
Netherlands.



Dear Sirs,

European Patent Application 81303957.5  
Dansk Eternit-Fabrik A/S

It has come to our notice that the specification contains an obvious error and we therefore respectfully request that the following correction may be made under the terms of Rule 88:-

Page 16 line 7 - delete "sili sol" and substitute  
"silica sol".

We enclose an additional copy of this letter and should be glad if it could be returned to us as confirmation of safe receipt.

Yours faithfully,

A. J. M. Robinson,  
Authorised Representative.

The request for correction is allowed under  
R. 88 EPC / with the exception of the deleted  
points!.

THE HAGUE, 06. 11. 81  
RECEIVING SECTION

RJ

Partners:	E. W. L. M.
G. F. Arthur	P. L. B. - a
M. I. Koo	G. N. B. - c
A. J. M. Robinson	C. D. N. K. - e
K. D. N. Keeney	Accounts
V. E. Broome	R. W. M.



European Patent  
Office

## EUROPEAN SEARCH REPORT

**0047158**

Application number

EP 81 30 3957.5

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<b>DE - A1 - 3 002 484 (AMIANTUS AG)</b> * claims * <b>&amp; GB - A - 2 042 607</b> —	1-7	C 04 B 29/04 C 04 B 31/02 C 04 B 13/21 C 04 B 31/34
P,E	<b>EP - A2 - 0 033 796 (CAPE BOARDS &amp; PANELS LTD.)</b> * page 3, lines 25 to 35, page 4, lines 11 to 15 * —	1-3	
A	<b>GB - A - 2 037 837 (TURNER &amp; NEWALL)</b> —		TECHNICAL FIELDS SEARCHED (Int. Cl.)
A	<b>GB - A - 1 511 270 (OWENS-CORNING FIBER-GLAS CORP.)</b> —		C 04 B 13/00
D	<b>DE - A1 - 2 819 794 (DANSK-ETERNIT-FABRIK)</b> <b>&amp; US - A - 4 261 754</b> —		C 04 B 29/04 C 04 B 31/00 C 04 B 43/00
D	<b>EP - A2 - 0 012 546 (TURNER &amp; NEWALL)</b> —		
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			& member of the same patent family. corresponding document
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
Berlin	28-10-1981	HÖRNER	